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HISTORICAL FUEL REPROCESSING AND HLW MANAGEMENT IN IDAHO

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PURPOSE

The Idaho Chemical Processing Plant (ICPP) was constructed on the site of the National Reactor Testing Station, which is now the Idaho National Engineering and Environmental Laboratory (INEEL), and has stored and reprocessed irradiated nuclear fuel since 1953 to recover uranium 235, neptunium 237, and krypton 85 for the U.S. Department of Energy and its predecessor agencies.¹⁻³ The primary focus of the reprocessing at ICPP was on fuels that contained highly enriched uranium for recovery of the fissile uranium with no plutonium recovery. The fuel reprocessing included multiple head ends to process aluminum, zirconium, stainless steel, and graphite-clad fuels. Rather than be neutralized and stored in carbon steel tanks, as was the common practice at that time, the resulting acidic high-level liquid radioactive waste (HLLW) has been stored in stainless steel, 1100-cubic metre, single-shell tanks in underground concrete vaults. A solidification process was developed to form a granular calcine solid from the acidic HLLW with a sevenfold volume reduction using the waste calcining facility (WCF) and the new WCF (NWCF). The calcined waste is stored in near-surface, stainless steel bins within concrete vaults. Glass and glass-

ceramic formulations were developed to immobilize ICPP calcines.

This article reviews some of the key decision points in the historical development of spent-fuel reprocessing and waste management practices⁴ at ICPP that have helped ICPP to successfully accomplish its mission safely and with minimal impact on the environment.

ICPP REPROCESSING DEVELOPMENT

The ICPP was located on an arid tract of withdrawn public land previously used by the U.S. Navy for testing guns and munitions. The development of the initial plant processes and the initial design scoping of the plant were carried out by Oak Ridge National Laboratory (ORNL). After completion of the design studies, the Atomic Energy Commission Processing Advisory Committee recommended in April 1950 that the plant be built at the National Reactor Test Site, a precursor of INEEL, in Idaho. In June 1950, the Foster Wheeler Corporation was selected as the architect-engineer with responsibility for all detailed plant design except for the processing equipment. The American Cyanamid Company was selected as the operating contractor in late 1950, and the Bechtel

Corporation was selected as the construction contractor. Excavation started in 1950, and construction was complete in mid-1952. After a preliminary test, cold run, and low-radiation-level-run period, the plant was placed in routine production in March 1953. Late in 1953, Phillips Petroleum Company assumed responsibility for plant operation.¹ The original main processing building at ICPP is shown in Fig. 1 and consists of 29 cells, each typically 20 feet square and 28 ft deep. The bottom of the cells was lined with stainless steel, and maintenance was accomplished by direct contact after decontamination. With the exception of four cells, which had viewing windows and manipulators, the in-cell equipment was controlled remotely from an operating corridor that ran the length of the building between two rows of cells. Figure 2 is a 1956 photograph of the completed reprocessing and fuel storage facilities and location of the underground HLLW storage tanks.

The ICPP was designed for the processing of highly enriched uranium fuels³ from more than 100 reactors, including aluminum, zirconium, stainless steel, and graphite fuel types. Aluminum-based fuel was typically dissolved⁵ in nitric acid using a mercuric nitrate catalyst; zirconium-based fuel was typically dissolved in hydrofluoric acid, which was subse-

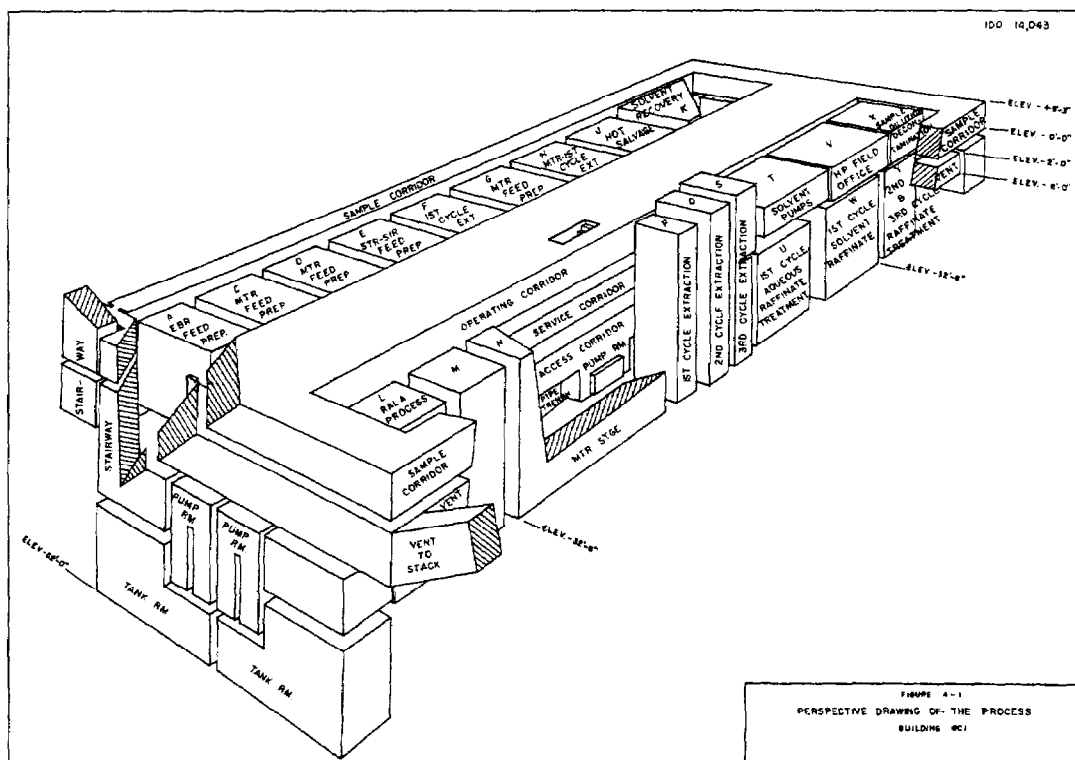


Fig. 1. Drawing perspective of ICPP fuel-reprocessing-plant building CPP 601

quently complexed with aluminum nitrate while using soluble neutron poisons to control criticality; stainless steel-based fuel initially used sulfuric/nitric acid dissolution and later used electrolytic dissolution in nitric acid containing gadolinium as a neutron poison. Graphite-based fuel was processed by combustion of graphite followed by nitric and hydrofluoric acid dissolution of the resulting ash. Low-level wastes from throughout ICPP were collected, concentrated through evaporation, and transferred to the liquid waste tanks. Figure 3 illustrates the ICPP processing flow sheets, including the multiple head-end dissolution processes.

In the recovery of highly enriched uranium, ICPP began reprocessing Hanford aluminum fuel⁶ in the batch aluminum dissolution facility in 1953. In 1955 the facility was modified for continuous aluminum dissolution.⁷⁻¹⁰ A batch zirconium dissolver¹¹ was operational in 1956, and stainless steel dissolution using sulfuric acid^{12,13} was developed in 1956. Semicontinuous zirconium dissolution using the soluble poison (boron) was developed¹⁴ in 1965. A coprocessing flow sheet was developed to use the aluminum nitrate from the aluminum fuel dissolver solution to complex the fluoride from the zirconium dissolver solution to minimize the addition of process reagents.¹⁵ Electrolytic dissolution of stainless steel fuel

in nitric acid using soluble gadolinium poison¹⁶⁻¹⁹ replaced the Carpenter-20 stainless steel dissolver in 1971. Processing of graphite-based Rover fuel was initiated²⁰⁻²² in 1983. A new zirconium-based dissolution process, the fluorinel dissolution process (FDP), was constructed in 1986 as part of the fluorinel and storage facility (FAST) and used viewing windows, manipulators, and a crane for remote operation and remote maintenance.²³ The FDP used cadmium and/or boron-soluble poisons in reagents that included hydrofluoric acid, nitric acid, and aluminum nitrate in three batch dissolver and complexer trains operating in parallel. A custom processing facility was operated to process small to moderate quantities of fissile material from a variety of fuels that could not be processed by conventional facilities and equipment.²⁴ A total of 31 432 kilograms of uranium containing highly enriched uranium 235 was recovered at ICPP from 1953 through 1991. The amount of recovered uranium for each category is described in the following as category/kilogram of uranium: aluminum/15 636, zirconium/5403, stainless steel/6036, graphite/3028, and custom processing/1329.

Neptunium 237 was first recovered from the fuel dissolver product in 1965, and the solutions were stored until it was purified and shipped²⁵ in 1972. Barium

140 was recovered at the ICPP as a special isotope and source of a short-lived high-gamma-producing lanthanum 140 by rapid turnaround processing of Materials Testing Reactor (MTR) fuel.²⁶

A rare gas plant with the capability of recovering fission product xenon and radioactive krypton 85 from fuel dissolver off-gases was constructed as part of ICPP. The first process used liquid nitrogen-cooled carbon beds to capture the noble gases from the aluminum dissolver off-gases.^{27,28} The carbon beds were replaced in 1958 with a more efficient cryogenic distillation process.^{29,30} An ambient-temperature hydrogen recombiner was added in 1978 to permit noble gas recovery

from the zirconium fuel dissolver off-gas containing hydrogen. More than 100 000 curies of krypton 85 and 8000 litres of fission product xenon were captured after the restart and upgrade of the rare gas plant in 1968.

The dissolver effluent from the dissolution facilities contacted organic solvent countercurrently in three different extraction cycles.^{2,31} The basic process used tributyl phosphate in normal paraffin hydrocarbon to extract uranium from the dissolver effluent. The second and third cycles used hexone for improved product purity. Before 1969, the uranyl nitrate was packaged and shipped to fuel fabrication facilities. After 1969, the concentrated uranyl nitrate was converted to uranium trioxide, prior to shipment, using a fluidized-bed process developed and implemented³² at ICPP. The raffinate from the solvent extraction process [the high-level waste (HLW)] was transferred to liquid waste storage tanks.

Additional details of the different fuel dissolution head ends follow.

Batch Aluminum-Uranium Dissolution

The first fuels processed at ICPP were uranium slugs from Hanford in 1952 followed by fuels from the Experimental Breeder Reactor (EBR)-I and uranium-aluminum alloy fuels⁶ from MTR. Separate dissolution, feed adjustment, and

feed solution storage facilities for EBR-I fuel had been designed as a portion of the original plant. The equipment was first checked by cold runs during the preoperation testing period in 1952. Runs conducted in July 1954 used depleted uranium slugs and pieces of aluminum tubing charged to the EBR dissolvers. New flow sheets were prepared for the EBR "hot" runs conducted in 1955 because of larger than anticipated EBR slug charges. The EBR-I core fuel elements consisted of several short pieces of enriched uranium rod enclosed in stainless steel tubing. Natural uranium slugs were placed in the tubing above and below the enriched material for breeding. The stainless steel outer shell was cut from the slugs, and the slugs were put in aluminum tubes at the reactor before transfer to ICPP. Because of low burnup (approximately 0.2 percent), only two extraction cycles were required for the EBR-I fuel to purify the uranium. The hot full-scale production runs were successful in dissolving the fuel and decontaminating the uranyl nitrate to "exceptional radiochemical quality," with a total uranium recovery of more than 2740 kg.

Continuous Aluminum-Uranium Dissolution

Aluminum-clad fuel from university and test reactors throughout the world was processed using continuous dissolution⁷⁻¹⁰ at ICPP. Continuous aluminum dissolution using nitric acid and mercuric nitrate catalyst was run from 1955 until 1992, when reprocessing was curtailed. Early development in support of the continuous dissolver used a "tall" 5-centimetre (2-inch)-diameter stainless steel pipe with a cooling section at the top. The acid feed was continuously steam heated to near-boiling temperatures. The product was water cooled and collected in a stainless steel drum. The reactor fuel material charged to the dissolver was simulated slugs, 3.8 cm (1.5 in.) in diameter and 20.3 cm (8 in.) long. Extruded aluminum bar stock and cast and extruded slugs were used in the initial experimental work. Marked differences were observed in the dissolution rates of cast and wrought alloys. At constant acid feed conditions, dissolution rates varied with the cube root of catalyst (mercury) concentration. A simulation of the process was reported,³³ and a new cata-

lyst for a nitric acid dissolution process, which avoided using the mercury catalyst, was patented.^{34,35} The total amount of uranium recovered using continuous aluminum-uranium dissolution was less than 12 896 kg.

Batch Zirconium Dissolution

Zirconium fuel is resistant to nitric and hydrochloric acids and has limited solubility in sulfuric acid.¹¹ Therefore, hydrofluoric acid was used for dissolution of zirconium-based fuel, and Monel was used as the material of construction for the dissolver. The zirconium-hydrofluoric acid reaction liberates hydrogen gas, which was controlled to remain below the explosive limit by controlling the rate of acid addition to the dissolver and by purging with nitrogen, which also reduces dissolver corrosion. A feed adjustment step using chromic acid and then aluminum nitrate oxidizes the uranium to the VI valence state, complexes excess fluoride, and supplies nitrate ion salting strength for adequate extraction. The cold production runs using unirradiated fuel assemblies tested the chemistry and equipment of the proposed

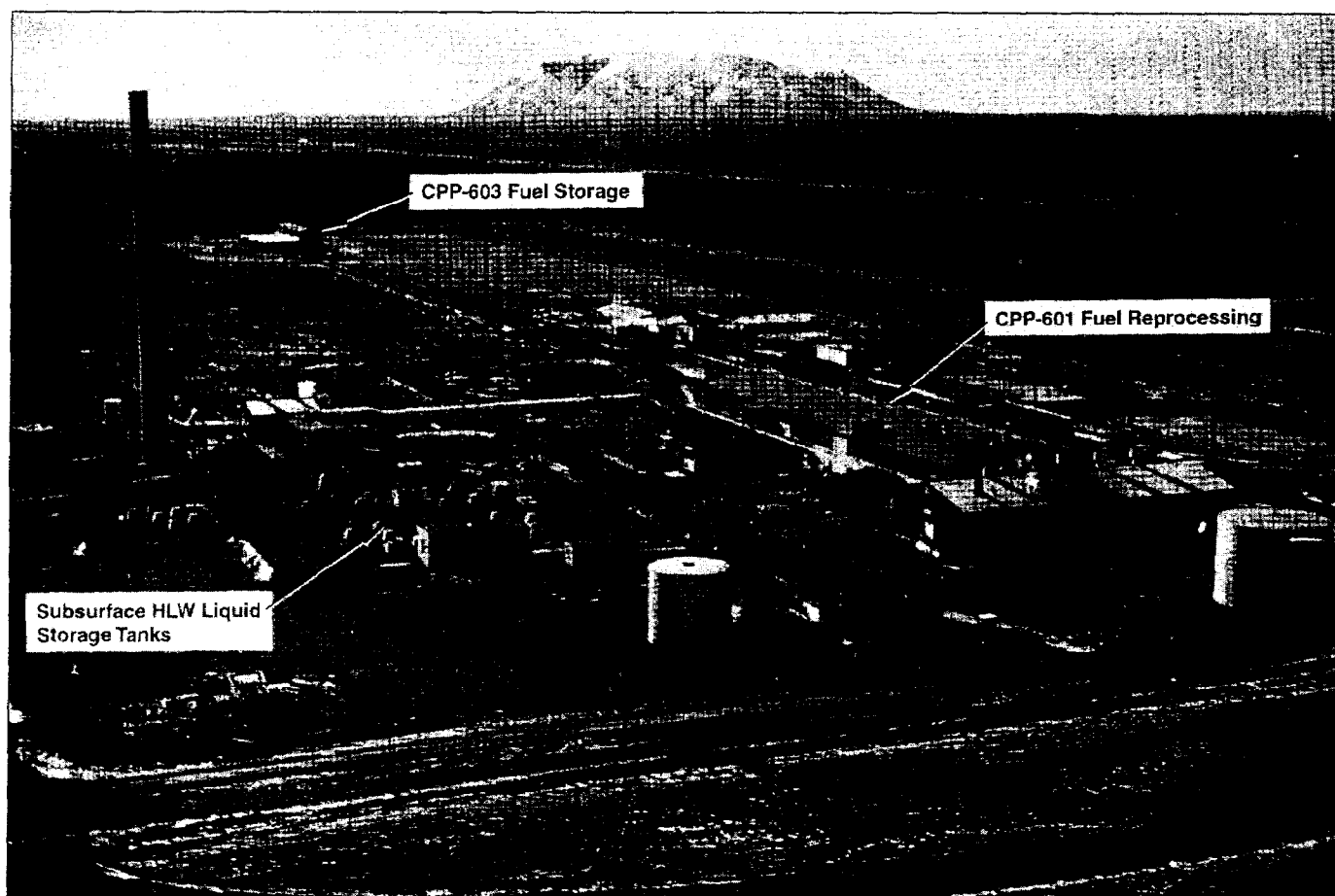


Fig. 2. A 1956 photograph of fuel storage building CPP 603, fuel-reprocessing building CPP 601, and location of underground HLW tank storage

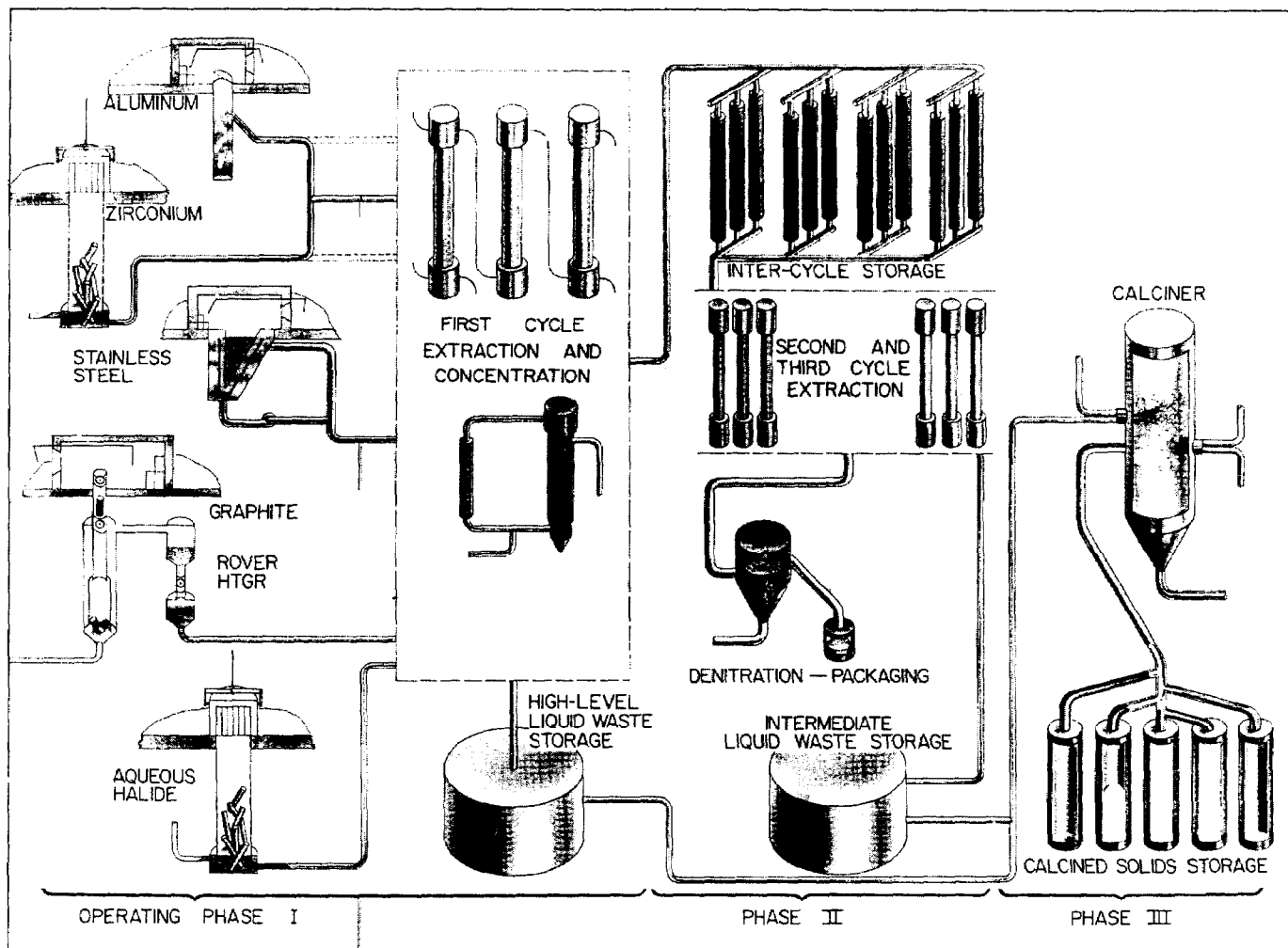


Fig. 3. ICPP processing flow sheets, including the multiple head-end dissolution processes

flow sheet. Hot operation of the batch zirconium dissolution from 1956 until 1965 resulted in recovery of 68 kg of uranium.

Batch Stainless Steel Dissolution

A small amount of submarine intermediate reactor (SIR), organic moderated reactor experiment (OMRE), and Vallecitos boiling water reactor (VBWR) fuel was successfully reprocessed using sulfuric acid to dissolve stainless steel-bearing fuel^{12,13} between 1956 and 1970. In the SIR process, the fuel elements were dissolved in sulfuric acid. Nitric acid was then added to dissolve the uranium oxide, to inhibit corrosion of downstream stainless steel by the dissolved product, and to provide salting strength for the extraction. The dissolver was 15.2 cm (6 in.) in diameter and 8.2 metres (27 ft) high with a working volume of 75 L. Carpenter-20 was selected for the dissolver material. A total amount of 136 kg of uranium was recovered using batch stainless steel dissolution.

Semicontinuous Zirconium Dissolution with Soluble Poison

Highly enriched zirconium-uranium alloy fuels were processed continuously beginning in 1965 at ICPP in the first campaign in which a soluble neutron poison (boron) was used for primary criticality control, which also resulted in processing rates up to tenfold greater than for previous zirconium-processing campaigns.¹⁴ A boron monitor was developed to ensure that 3.8 grams/L of boron was present at all times. The monitor consisted of two BF_3 neutron detector tubes immersed in the dissolvent makeup tank with a Pu-Be neutron source. The neutron detector tubes were located 11.4 cm (4.5 in.) from the source. (The original ICPP zirconium dissolver was limited to 1700 g of total uranium before burnup. Equipment downstream of the original dissolver was safe by geometry.) An average of about 600 kg of zirconium was charged to a slotted basket inside the 106.7-cm (42-in.)-diameter Monel dissolver. The original bell-shaped dissolver was replaced in 1978 with an an-

nular design, increasing the capacity by 25 percent. Dissolver product overflowed continuously from the dissolver and was transferred to a feed adjustment tank for continuous complexing with the aluminum nitrate solution. A total amount of 3789 kg of uranium was recovered using semicontinuous zirconium dissolution with soluble poison from 1965 to 1986.

A coprocessing flow sheet was developed to minimize waste generation by replacing the addition of aluminum reagent required to chemically complex the fluoride from the zirconium semicontinuous dissolution with aluminum nitrate generated from the aluminum dissolver. The resulting fluoride-containing stream could then be contained in the stainless steel piping without excessive corrosion and with a minimum addition of process chemicals.¹⁵

Electrolytic Dissolution of Stainless Steel-Clad Fuel

A process was initiated in 1973 for stainless steel-based fuels¹⁶⁻¹⁹ primarily

from EBR-II. The fuel was placed in a nitric acid-flooded electrically inert niobium basket between a titanium cathode and a platinum anode. Under a direct current, the stainless steel becomes anodic, dissolves in nitric acid, and is compatible with subsequent solvent extraction. The pilot-plant dissolver simulated a 10.1-cm (4-in.) section of a plant-scale unit. In this dissolver, fuel elements were charged horizontally into a basket placed between the electrodes. The nitric acid solution was supplied equally to the anode and cathode sides near the bottom of the dissolver and flowed out near the top of the dissolver with the off-gas. The electrolyte was continuously recirculated to the bottom of the dissolver after being passed through a cooler.

The 18 pilot-plant test runs with simulated and actual fuel element sections showed adequate dissolution rates and process control for processing highly enriched stainless steel and Nichrome cermet fuel. The first processing campaign, completed during the first four months of 1973, resulted in recovering 1500 kg of uranium (52.5 percent enriched) from EBR-II fuel and scrap. Dissolution proceeded entirely as expected, and the use of gadolinium as a nuclear poison proved entirely satisfactory. The total quantity of uranium recovered using electrolytic dissolution of stainless steel-clad fuel was 5900 kg.

Graphite-Based Rover Fuel Processing

Hot operations were initiated in 1983 to recover uranium from graphite matrix rocket (Rover) fuels.²⁰⁻²² The process developed at ICPP was based on charging whole fuel elements to the primary burner (to avoid having to crush the elements), burning the graphite continuously in a fluidized-bed burner, elutriating the metal oxides for collection and subsequent charging to a batch secondary burner for complete combustion of graphite and collection of the resulting ash, and dissolving the secondary burner ash using nitric and hydrofluoric acid. The nitric acid sufficiently dissolved U_3O_8 , but complex niobium-uranium compounds in the form of Nb_3UO_{10} (about 10 to 15 percent of the uranium) required hydrofluoric acid for dissolution. Extensive development of primary and secondary burner concepts was undertaken. The ash dissolution step involving hydrofluoric acid mixed with nitric acid required a special plastic, Kynar™ dissolver. Special techniques developed to reduce erosion in transfer

lines included blinded tees and elbows. The process was successful in recovering about 3027 kg of uranium through 1984.

Fluorinel Fuel Processing

Hot operation of the fluorinel dissolution process²³ (FDP) began in 1986. The process chemistry, the performance of the equipment, and the nuclear safety of the system were all successfully demonstrated during the first year of operation. The primary purpose of the FDP was to dissolve spent Zircaloy-clad Naval reactor fuels in preparation for the recovery of unused uranium. The FDP process developed at ICPP consisted of three dissolver-complexer trains, each operating batchwise. The batch process was necessary to allow implementation of new step controls for criticality safety in large-diameter dissolvers (with 91.4-cm or 3-ft diameters) and complexers (with 167.6-cm or 5.5-ft diameters). Criticality safety was ensured in these vessels using soluble neutron poisons in reagents and limiting the mass of uranium 235 to 12.9 kg per train. Cadmium was used for the poison in all reagents except hydrofluoric acid, which used boron because of solubility requirements. The process was successful in recovering greater than 99.5 percent of the uranium from each batch. Development of the chemical flow sheet required a delicate balance between corrosion control in the Hastelloy C-4 dissolvers and precipitate formation. The complexing step required determination of the zirconium-fluoride complexing constants and development of a titanium electrode^{36,37} to measure free HF. A total amount of 1546 kg of uranium was recovered using the FDP.

ICPP WASTE MANAGEMENT CONSIDERATIONS AND DESIGN DECISIONS

Increasing liquid waste volumes were projected as more and more fuel was committed for reprocessing. Basic decisions were made that resulted in a different approach than at the other DOE reprocessing sites; the following issues⁴ ensued.

Neutralization of the Acidic Raffinate

A decision was made *not* to neutralize raffinates with sodium hydroxide, as was commonly practiced in those days. This was possible because of the implementation of improvements in extraction tech-

nology. Neutralization would have significantly increased the volume of the HLLW generated and complicated its use as an isotope feedstock for ORNL's expanding isotope-recovery operations and would have precluded continuous fluidized-bed waste calcining because of the inability of the process to handle high concentrations of alkali nitrates present in the neutralized waste.

Design and Number of Liquid Storage Vessels

A limited number of 1100-m³ (300 000-gallon) waste tanks were constructed using stainless steel instead of carbon steel. Stainless steel was available after the end of World War II and was necessary because the waste was kept acidic. The initial tanks were constructed of Type 348 stainless steel. Corrosion testing was used to justify the substitution of more economical Type 304L stainless steel in future tank construction. Tanks planned for use with HLW were equipped with in-tank cooling systems to maintain the solution at a low temperature, which minimized material corrosion. Acidic waste with no precipitates minimized the formation of galvanic corrosion cells between solution precipitates and the tank material. Two tanks were constructed at the start of reprocessing, and the current number of 11 tanks was completed in 10 years. As a consequence of the waste calcination process, no more liquid waste tanks were required for the 30+ years of fuel reprocessing. No tank failures have been experienced, even for tanks used to store aluminum-complexed-fluoride solutions.

Selection of Calcination Process

Initially the liquid extraction raffinate was primarily aluminum nitrate. Candidate solidification processes included pot calcination, spray calcination, and rotary kiln calcination.³⁸ Later the fluidized-bed process was chosen because it was continuous, was readily adaptable to remote operations, had no moving parts to wear out, had adequate throughput capacity to meet ICPP requirements, and was adequately developed for the demonstration.³⁹

Design and Construction of Calcined Solids Storage Bin Sets

Calcined solids were stored in stainless steel bins with extended design lives. The vessel design was based on a critical centerline temperature that would prevent the radionuclide migration. The first calcined solids storage facility (CSSF) was conservatively designed and constructed

of annular bins; subsequent CSSFs incorporated observed heat transfer experience and employed a more economical cylindrical bin design. After CSSF 1, subsequent CSSFs were designed with retrieval ports and access for future retrieval to allow for subsequent processing.

CALCINATION TECHNOLOGY DEVELOPMENT

The concept of calcining radioactive liquid waste by atomizing the liquid in a heated bed of inert particles was originated by Argonne National Laboratory (ANL). Early development by ANL consisted of brief feasibility studies using a 7.5-cm (3-in.)-diameter calciner and additional more extensive studies using both unshielded and shielded 15-cm (6-in.)-diameter calciners.^{40,41} Tests with the 7.5-cm-diameter calciner were all with cold feed. Subsequent tests with the 15-cm-diameter calciners were both cold and up to 12 percent spiked, hot, as-produced feed from ICPP primarily to test the behavior and treatment of fission products in the calcination process. Initial development was based on testing the acidic aluminum nitrate solution and was later extended to include Hanford-type PUREX waste. The ANL pilot-plant experience indicated that the fluidized-bed process was feasible and that ruthenium was the only volatile fission product. The tests showed that virtually all activity except ruthenium remained in the solid product over the temperature range of 350 to 550°C. At a 350°C operating temperature, about 88 percent of the ruthenium was volatilized, whereas at 550°C, less than 1 percent was volatilized. Both sintered metal filters and venturi scrubbers, in which the scrub solution was recycled to the feed to minimize additional waste streams, were tested for removing particulates from the off-gas; silica gel adsorbers were tested for removing volatile ruthenium. Using the ANL 15-cm (6-in.) calciner, venturi scrubbers and silica gel were found to be very effective in removing particulates and ruthenium, respectively, from the off-gas. Tests also showed that the silica gel could be readily regenerated.

Pilot-plant testing at ICPP used a 15-cm (6-in.)-diameter pilot-plant calciner patterned after the one used by ANL but with a number of changes to provide equipment and process scaleup data and to define process parameters for designing the demonstration waste calcining facility^{42,43} (DWCF). The 15-cm-diameter

calciner vessel was 1.7 m (5.5 ft) long and contained a charging tube, a thermowell, and an off-gas tube at the top of the vessel. The calcined product was removed continuously by means of a 1-in. drawoff line extending 61 cm (2 ft) above the distributor plate. Heat was supplied by 18 internal electric heaters with 15-cm (6-in.) heated lengths located horizontally inside the calciner bed. Liquid feed was introduced under pressure through commercially available pneumatic atomizing spray nozzles. To provide operating data, pressure taps and thermocouples were located throughout the bed. Calciner auxiliary equipment included a cyclone, a spray scrubber, a condenser, and a fluidizing gas preheater. Operating variables studied were feed rate, bed temperature, fluidizing velocity, feed nozzle air-to-feed ratio, product drawoff, and liquid feed composition. A problem with size distribution not reaching steady state made it difficult to determine various effects of operating variables on the product.

It was generally determined that feed rate influenced particle-size distribution and possibly bulk density. Low feed rates generally produced smaller particles than at higher rates. The effect of feed rate on bulk density was not conclusive. The bed temperature measurements showed decreasing bulk density with increasing bed temperature throughout the temperature range studied. The bed temperature also had a profound effect on particle-size generation. Low bed temperatures (300°C) produced large mass mean particle diameters, whereas 500°C tended to produce fines. Changing fluidizing velocity appeared to change particle-size distribution. Runs were made at constant air-to-feed rates, but low atomizing air flow rates possibly caused agglomeration tendencies. A relatively small amount of air was passed countercurrent to product overflow. The air was found to be an effective means of controlling particle-size withdrawal. The concentration and composition of feed to the calciner was not studied but was expected to have a strong effect on calcine structure and size distribution. Although most runs were made with aluminum fuel, some exploratory runs were made with stainless steel and zirconium-type fuel raffinates.^{42,43}

The results of the pilot-plant tests verified the feasibility of calcining aluminum-type waste. The advantages of the technology include independence from complicated moving parts, excellent control of bed temperature with uniform high heat transfer rates, reduction in the

corrosion potential of the stored product, adaptability to remote operation, and excellent control of particle size and properties.

ICPP CALCINATION DEMONSTRATION AND HOT OPERATIONS

Pilot-plant tests were successful and established target ranges of principal operating values for a full-scale demonstration, which included the following: (a) calciner bed temperatures of 400 to 500°C, (b) fluidizing air velocities of 23 to 40 cm/second (0.75 to 1.3 ft/s), and (c) air-to-liquid volume ratios of 500 to 750 through the feed nozzle. The DWCF was constructed at a cost of \$6 million from 1958 to 1961. A major portion of the equipment, about 70 percent, is for off-gas cleanup. The cleanup equipment includes a cyclone, a quench tower, a venturi scrubber, entrainment separators, silica gel adsorbers, and high-efficiency particulate air filters. Calcium nitrate was added to fluoride-bearing zirconium-type waste to react with fluoride and to reduce corrosion on downstream process equipment and piping by controlling fluoride volatility. The granular calcined solids product was pneumatically transferred to and stored in vented stainless steel bins located in concrete vaults.

The WCF calciner vessel was 1.2 m (4 ft) in diameter. Radioactive feed was introduced into the bed through pneumatic atomizing nozzles. The feed was sprayed through three nozzles equally spaced in a horizontal plane at a total net processing rate of 320 L/hour (85 gal/h), including waste, additives, and scrub recycle. During the first three campaigns and until June 1969, heat was supplied by an in-bed heat exchanger bundle using a sodium-potassium alloy that operated at a bundle temperature of 400°C. The NaK was pumped by an electromagnetic pump and heated in an oil-fired furnace. Preheated fluidizing air was introduced through 14 capped orifices equally spaced on a distributor plate. Operation at superficial fluidizing velocities between 25 and 40 cm/s (1.0 and 1.3 ft/s) was satisfactory with average bed particle size ranging from 0.6 to 0.75 millimetres.

Cold testing began in 1961 and continued for 1½ years. In November 1962, operation of the DWCF was demonstrated, and the facility became known as the WCF. Radioactive feed was introduced on 8 December 1963. The first run

electromechanical manipulators and at NWCF were first tested in a full-scale mockup facility at INEEL and positioned for easy removal and replacement without lengthy shutdowns or high-radiation exposures to personnel. Failed equipment was transferred directly to integral shielded facilities for remote decontamination and subsequent repair or disposal. NWCF operating experience has demonstrated the effectiveness of this concept and design. Figure 4 shows a 1985 photograph of the WCF, NWCF, and calcined storage bin sets numbers 1 through 6, and location of subsurface HLW storage tanks.

The NWCF began hot operations in September 1982 after extensive system operability and cold testing and calcined 6000 m³ (1.6 million gal) of waste before shutting down in March 1984 when all available liquid waste feed was processed. During the down period, a new distributive control system was installed. The NWCF was restarted on 30 September 1987, and has operated successfully on various feeds and combinations of feed such as fluorine, zirconium, and blended fluorine-sodium waste feeds. To date, the NWCF has calcined more than 12 100 m³ (3.2 million gal) of radioactive liquid waste to 1670 m³ (59 000 ft³) of calcined solids. Successful combined opera-

The WCF operated until March 1981, calcining about 15 000 m³ (4 million gal) of liquid radioactive waste.⁴⁵

NWCF DESIGN, CONSTRUCTION, AND OPERATION

The NWCF was designed to replace the WCF because of the increased time required for maintenance of the WCF without remote capabilities and the need to increase throughput to accommodate increased fuel shipments.⁴⁶ The construction incorporated many improvements. The calciner vessel active bed region was increased to a 1.5-m (5-ft) diameter with a 2.1-m (7-ft)-diameter expanded upper section fabricated from Type 347 stainless steel. Sizes of downstream vessels were also increased, and the design net processing rate was increased to 11 300 L/day (3000 gal/day). A more corrosion-resistant alloy, Ni-fluoride and trace chloride) chemical environments and high operating temperatures. Because of the WCF experience, high-maintenance equipment (pumps, valves, flanges, electrical connections, and off-gas filters) was placed in corridors readily accessible for remote replacement using master-slave and

lasted 11 months, until 15 October 1964, when the first CSSF was filled. More than 1800 m³ (500 000 gal) of radioactive liquid waste from three waste tanks was converted to 210 m³ (7500 cubic feet) of solids. The net output exceeded the design rate by 15 percent, and the process operated at 99 percent efficiency. As fuel shipments to ICPP increased, additional CSSFs were built, and the WCF was modified for higher feed rates. To allow increased WCF capacity and reliability, an in-bed combustion system using oxygen-atomized kerosene was installed⁴⁴ in 1970. The use of in-bed combustion increased the operating temperature to 500°C and resulted in increased heat transfer rates, a change in the behavior of fission product ruthenium, and lower metal wall temperatures. A less volatile ruthenium species reduced concentrations in the off-gas by a factor of 100 to 200. However, decontamination on WCF internal surfaces became more difficult. Boric acid was added batchwise to the aluminum nitrate feed solution to suppress the formation of alpha alumina and to ensure that the product would remain in the amorphous rather than the crystalline form. Boric acid also helped to control particle size; minimize decontamination problems; and reduce corrosion of pumps, valves, and piping by making the aluminum species soluble in

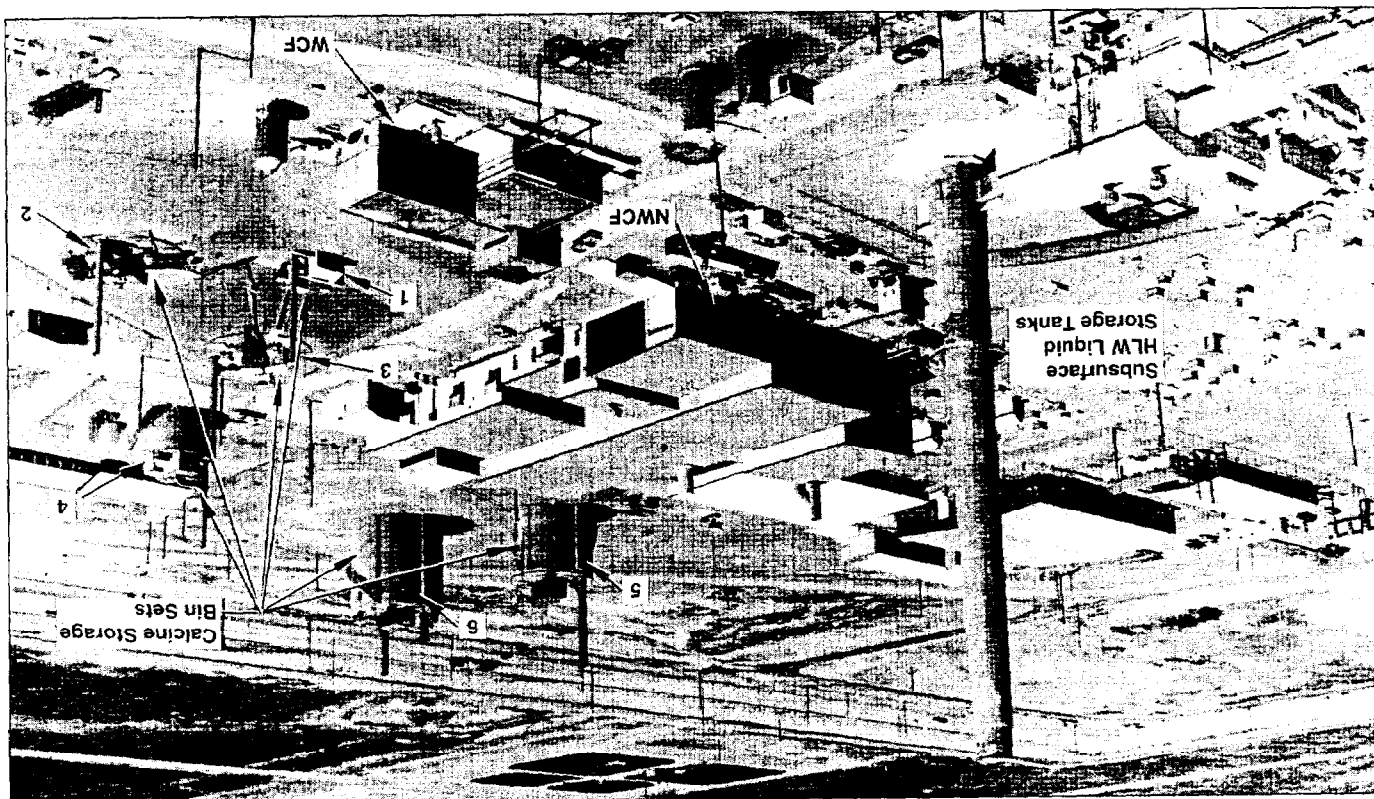


Fig. 4. A 1985 view of ICPP waste storage and waste-processing facilities

tion of the NWCF and WCF has eliminated the need to build twenty-six 1100-m³ (300 000-gal) waste tanks to assume acidic waste storage.^{47,48} If the practice of neutralization had been used to manage the ICPP HLLW, up to a 7.5-fold increased storage volume would have been required, or 195- to 1100-m³ tanks (equivalent to 65 Hanford million-gal tanks).⁴⁹

HLW IMMOBILIZATION TECHNOLOGY DEVELOPMENT

As calcining of acidic HLLW became a reality, it became readily apparent that methods for final disposal of the calcined waste must be developed.⁵⁰ The reprocessed HLW at ICPP consists of varied nuclear-fuel compositions and is also different from that of either the Hanford or Savannah River HLW. The major differences are that (a) the liquid waste is acidic as opposed to neutralized (basic) and (b) the ICPP waste compositions are totally different. The ICPP calcined wastes are derived mainly

from cladding material. Waste from the early 1960s consists mainly of aluminum, whereas later reprocessed waste contains as primary constituents zirconia, calcium fluoride and alumina, and other constituents such as alkali and other metals. The calcine, although physically and thermally stable, was leachable for several of its radioactive constituents, most notably cesium. Currently, the inventory of 3800 m³ of HLW calcine at ICPP consists primarily of alumina and zirconia-based calcines, resulting from dissolution of aluminum and zirconium fuels, respectively, and zirconia-sodium blends. The amounts of alumina, zirconia, zirconia-sodium, and fluorine-sodium calcines are approximately 560, 1250, 950, and 800 m³, respectively. The major component (in weight percent) in ICPP HLW alumina calcine includes alumina (82 to 95), and the major components (in weight percent) in zirconia calcines and zirconia calcines blended with other sodium-bearing process and decontamination wastes include fluorite (41 to 44), zirconia (17 to 19), calcia (12 to 13), alumina (9 to 14), alkali oxides (5 to 7), borate (2 to 4), and cadmium oxide (0 to 7). Fission product content is typically less than 1 weight percent. An additional 240 m³ of calcine inventory consists of calcines from processing other minor fuels and startup bed material.⁵¹

Because the calcines at ICPP are of varied composition, a practical and simple computer code was developed not only to predict glass stability but also to determine a practical glass composition for a proposed waste composition. The code has worked effectively to determine aspects of permissible waste loading, immobilized waste durability, and amount and type of additives needed.⁵²

Glass Waste Forms

Preliminary scoping tests were run in the 1960s, and laboratory testing was started in the 1970s to develop glass formulations for ICPP calcines. Using fully radioactive calcine,⁵³ a phosphate glass was prepared in the mid-1960s with the following components in weight percent: alumina calcine, 25; P₂O₅, 40.5; Na₂O, 18.6; and PbO, 15.9. Leaching rates were measured using continuously circulating distilled water at 25 and 94°C and were not changed with a devitrified sample. Other early waste forms that were studied in the late 1960s included calcine

particle coating with molten aluminum and steel spray and matrix encapsulation in metal, glass, plastic, or grout.⁵⁴ In the 1970s, glass formulations were tested further. For alumina calcine, waste loadings of up to 29 and 24 weight percent could be obtained in a borophosphate⁵⁵ and borosilicate⁵⁶ glass, respectively. For zirconia calcines, waste loadings of 33 weight percent were observed using a borosilicate frit. Laboratory- and pilot-scale melter experiments showed that the high zirconia-calcium fluoride glass can be produced at practical melter temperatures, and very durable melter refractories are required because of fluoride corrosiveness.^{57,58}

Nonradioactive laboratory- and pilot-scale and radioactive laboratory-scale tests were run using the borosilicate frit 127 (composition in weight percent: SiO₂, 70.3; Na₂O, 12.8; B₂O₃, 8.5; Li₂O, 6.2; and CuO, 2.1). Materials Characterization Center (MCC)-1 and MCC-2 leach tests⁵⁹ indicated that there did not appear to be significant differences in the glasses formed using simulated zirconia calcine at laboratory or pilot scale and using radioactive zirconia calcine at laboratory scale.⁵⁶

Glass-Ceramic Waste Forms

Waste-volume-reduction efforts resulted in the development of glass-ceramic

waste forms during the 1980s for the ICPP calcined⁵⁰ HLW. A glass-ceramic can accommodate up to about 70 weight percent calcine, whereas a glass can accommodate only about 30 weight percent calcine. In addition, the glass-ceramic is about 50 percent more dense. Therefore, final volume is greatly reduced, and the glass-ceramic is equally durable, if not more so. Processing a ceramic waste form is more sophisticated, ideally requiring a hot isostatic pressing (HIP) process and special particulate handling, blending, and containment technology.

To form durable glass and crystalline phases, glass-ceramic waste forms were prepared for various calcine compositions with the goal of effectively utilizing the refractory components, alumina, zirconia, and fluorite. Early testing was run with sintered glass-ceramics,⁶⁰ cold-press sintered ceramics,⁶¹ aluminum phosphate ceramics,⁶² and fluorapatite phosphate ceramics.⁶³ Polyphase glass-ceramic experiments were carried out for ICPP zirconia calcine waste compositions using a hot isostatic press for high-temperature sintering. Durable glass-ceramic forms could be made for zirconia calcine with additives, including silica, alkali, and yttria.⁶⁴⁻⁶⁶ Detailed microstructure analysis of these waste forms revealed the presence of cubic fluorite, monoclinic zirconia, stabilized cubic zirconia, tetragonal zircon, zirconolite, perovskite, and amorphous aluminosilicate phases. Normalized MCC-1 release rates⁶⁷ at 90°C of all major elements were less than 1 g/square metre·day.

Glass-ceramic formulations were also developed for zirconium-sodium-blended calcines using added borosilicate frit and other additives such as titania and metallic titanium and aluminum powders.⁶⁸⁻⁷³ Major crystalline phases included fluorite, zirconia, and zircon. Sphene, Ca₂Ti₇O₁₈, and other titanates were formed with added titanium, and nepheline and calcium-aluminum silicates were formed with the added aluminum. The higher amounts of metallic powder increased the amount of zirconia at the expense of zircon. MCC-1 leach rates decreased with decreased borate, and the lowest normalized elemental leach rates of less than 1 g/m²·day were found in the formulations containing 5 to 6 weight percent titanium and 2 to 3 weight percent aluminum. The amounts in weight percent of the crystalline phases were identified by X-ray diffraction as fluorite, 37; zirconia, 17; zircon, 14; and sphene, 16.

The reprocessed HLW at ICPP consists of varied nuclear-fuel compositions and is also different from that of either the Hanford or Savannah River HLW.

The major components in weight percent of the glass phase were identified by scanning electron microscopy as silica, 62; alumina, 19; and calcia, 19. The glass-phase components for the zirconia and zirconia-sodium calcines were found to lie in the phase stability triangle for silica, anorthite, and alpha-wollastonite.⁶⁷ Additional studies with similar calcine and frit composition were run to determine the effect of process soak time and added metal silicon and aluminum powders on the microstructure and durability.^{74,75} The lowest leach rates were found for the aluminum concentration at 2 weight percent and were found to increase with increasing silicon concentration. Constant leach rates were found for soak times of 4, 8, 16, and 24 h. Major crystalline phases were identified as fluorite, zirconia, and zircon. Minor phases of albite and anorthite were also identified.⁷⁵

A full 2^3 factorial design with a center point experiment was performed to investigate the effects of HIP time, temperature, and pressure on the durability of ICPP glass-ceramic forms using simulated zirconium-sodium calcine, borosilicate frit, and the additives TiO_2 and titanium. The results of the study indicate that higher HIP temperatures and longer HIP times improve leaching characteristics for many elements in experimental ICPP glass-ceramics.⁷⁶ Using the XSTAT statistical design software, a response surface methodology was tested for the processing variables, calcine particle size, HIP temperature, HIP time, calcine loading, amount of redox control additive, and mixing. Glass-ceramics based on titanium,⁶⁷ aluminum,⁷⁵ and phosphate⁷⁷ additives were tested, and the titanium formulation was found to be the most durable and the least sensitive to changes in processing variables.⁷⁸

Recent evaluations have proposed dissolution of calcine and separation of a small high-activity waste fraction, followed by a significantly smaller-scale vitrification process. The low-activity waste would be disposed on-site as a grout. Evaluations are continuing with a full-scale facility projected to process all of the calcine by 2035 to meet a legal agreement with the State of Idaho.^{79,80}

CONCLUSIONS

The ICPP fuel-reprocessing operation that began in 1953 has resulted in the recovery of 31 432 kg of highly enriched uranium and other by-products. The resulting HLLW was converted with a sevenfold volume reduction to approximately 3800 m³ of solid calcined HLW, which is stored safely in stainless steel bins with long design lives, and is scheduled for immobilization for shipment of the glass off-site by 2035. A set of decisions and focused development activities, including innovative fuel-reprocessing technologies, was developed during the history of ICPP and has resulted in these currently relatively safe conditions, with no major waste leaks to

By calcining and not neutralizing the HLLW, ICPP avoided the construction of up to 195 ICPP tanks or 65 Hanford-sized tanks and all of the potential problems associated with long-term HLLW storage.

the environment, which is not the case at some other DOE sites. By calcining and not neutralizing the HLLW, ICPP avoided the construction of up to 195 ICPP tanks or 65 Hanford-sized tanks and all of the potential problems associated with long-term HLLW storage. As a result, the HLW storage at ICPP currently represents relatively minimal environmental risk compared to other comparable DOE sites.

Some of the ICPP pioneering contributions include the following:

1. first to reprocess highly enriched uranium on a production basis
2. first to process breeder reactor fuels, the EBR-I Core I
3. first to dissolve spent nuclear fuel continuously on a routine schedule
4. first to use fixed and soluble neutron poisons for criticality control
5. first to operate a radioactive rare gas recovery plant in conjunction with a fuel recovery process
6. first to process stainless steel-alloyed fuel by sulfuric acid dissolution
7. first to recover uranium from high zirconium-uranium-alloy fuels by dissolution in hydrofluoric acid and to use an innovative coprocessing flow sheet for minimizing waste volumes
8. first to show that multiple head-end processing of various fuels is compatible with common second- and third-cycle purification
9. first to dissolve stainless steel-clad EBR-II reactor fuels using electrolytic dissolution
10. first to develop and implement the

production-scale fluidized-bed denitration of the highly enriched uranium product

11. first to develop and implement a production-scale calciner to solidify the HLLW.

ACKNOWLEDGMENTS

This work is sponsored by the DOE, Idaho Operations Office, under contract DE-AC07-94ID13223. The authors would like to acknowledge all of the pioneers who developed the processes and facilities and completed the successful reprocessing and waste management operations at INEEL.

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